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POSITIVE ELECTRODE ACTIVE SUBSTANCE AND NON-AQUEOUS ELECTROLYTE BATTERY
AND MANUFACTURING METHOD THEREOF

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[Claim 1] A positive electrode active substance characterized in that said active substance comprises a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) whose surface is covered with a fine particle as shown by the general formula LiFePO_4 .

[Claim 2] A non-aqueous electrolyte battery comprising a positive electrode containing a positive electrode active substance, a negative electrode containing a negative electrode active substance and a non-aqueous electrolyte which is present between said positive electrode and said negative electrode, which is characterized in that said positive electrode active substance comprises a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) whose surface is covered with a fine particle as shown the general formula LiFePO_4 .

[Claim 3] A manufacturing method of a positive electrode active substance characterized in that a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) and a fine particle as shown by the general formula LiFePO_4 are mixed and agitated at a particle temperature (T) in the range of $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$ in order to cover the surface of the said particle with said fine particle.

* Claim and paragraph numbers correspond to those in the foreign text.

[Claim 4] A manufacturing method of a non-aqueous electrolyte battery comprising a positive electrode containing a positive electrode active substance, a negative electrode containing a negative electrode active substance and a non-aqueous electrolyte which is present between said positive electrode and said negative electrode, which is characterized in that said positive electrode active substance is prepared by mixing a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) and a fine particle as shown by the general formula LiFePO_4 and agitating the above particle mixture at a particle temperature (T) in the range of $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$ in order to cover the surface of said particle with said fine particle.

[Detailed explanation of the invention]

[0001] [Technical area to which the invention belongs]

The present invention relates to a positive electrode active substance and a non-aqueous electrolyte battery using a lithium-nickel composite oxide and their manufacturing methods.

[0002] [Prior arts]

Recently, with a dramatic advance in various electronic devices, active research on a rechargeable secondary battery as a power source, which can be conveniently and economically used for a long time, has been in progress. As typical secondary batteries, a lead storage battery, an alkaline storage battery, a lithium secondary battery and the like, have been known. In particular, the lithium secondary battery has advantages

of high output power, high energy density and the like. The above lithium secondary battery comprises a positive electrode and a negative electrode which are capable of reversibly intercalating/deintercalating lithium ion, and a non-aqueous electrolyte solution.

[0003] In general, as the negative electrode active substance, a lithium metal, a lithium alloy, an electrically conductive polymer or a layered compound (carbon materials, metal oxides and the like) doped with lithium and an electrically conductive polymer or a layered compound (carbon materials, metal oxides and the like) which is in coexistence with a compound containing lithium, can be mentioned.

[0004] On the other hand, as the positive electrode active substance, metal oxides, metal sulfides, and polymers can be mentioned. For example, compounds which do not contain lithium such as TiS_2 , MoS_2 , NbSe_2 , V_2O_5 and the like, and lithium-containing composite oxides such as LiMO_2 ($\text{M} = \text{Co}$, Ni , Mn , Fe and the like) have been suggested.

[0005] As the electrolyte solution, a solution of a lithium salt dissolved in a non-protonic organic solvent such as propylene carbonate can be mentioned.

[0006] Furthermore, as the separator, polymeric films such as polypropylene are used. In this case, the film thickness is required to be as thin as possible from the standpoint of lithium ion conductivity and energy density. Normally, a separator with a film thickness of 50 μm or less is considered to be practical. A battery comprising the above-mentioned positive electrode and negative electrode and the

separator and the electrolyte solution which are present between electrodes can be used as a rechargeable secondary battery.

[0007] [Problem to be solved by the invention]

The Ni-type positive electrode active substance which increases the capacity of the lithium secondary battery loses a larger amount of lithium during charging than a conventional Co-type positive electrode active substance. As a result, the Ni-type positive electrode active substance loses its structural stability and causes capacity fade during charging. On the other hand, LiFePO_4 exhibits excellent structural stability and a lower degree of capacity fade. However, it has a problem of low energy density, which makes it difficult to be used alone.

[0008] To obtain a positive electrode active substance having favorable characteristics of excellent stability during charging and high capacity derived from both compounds, an attempt has been made to adhere LiFePO_4 to the surface of a Ni composite oxide particle. However, an effective method has not been obtained yet.

[0009] The present invention has been made based on the above-mentioned situation. That is, the purpose of the present invention is to provide a positive electrode active substance having favorable characteristics of high energy density derived from a Ni composite oxide particle and a low degree of capacity fade during charging derived from a LiFePO_4 particle, to provide a non-aqueous electrolyte battery using the above-mentioned positive electrode active substance and to provide their manufacturing methods.

[0010] [Means to solve the problem]

The positive electrode active substance of the present invention has a characteristic in that it comprises a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co), whose surface is covered with a fine particle as shown by the general formula LiFePO_4 .

[0011] In the above-mentioned positive electrode active substance of the present invention, since the surface of the particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ is covered with the fine particle as shown by the general formula LiFePO_4 , the above positive electrode active substance has favorable characteristics of high energy density derived from the Ni composite oxide particle and excellent structural stability derived from the LiFePO_4 particle.

[0012] Also, the non-aqueous electrolyte battery of the present invention comprises a positive electrode containing a positive electrode active substance, a negative electrode containing a negative electrode active substance and a non-aqueous electrolyte which is present between the above positive electrode and the negative electrode and has a characteristic in that the above positive electrode active substance comprises a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co), whose surface is covered with a fine particle as shown in the general formula LiFePO_4 .

[0013] In the above-mentioned non-aqueous electrolyte battery of the present invention, the positive electrode active substance comprises a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$, whose surface is covered with a fine particle as shown by the general formula LiFePO_4 . Therefore, it has favorable characteristics of high energy density derived from the Ni composite oxide particle and excellent structural stability derived from the LiFePO_4 particle. As a result, the non-aqueous electrolyte battery of the present invention using such a positive electrode active substance exhibits high capacity and excellent charging/discharging cycle characteristics.

[0014] Also, the manufacturing method of the positive electrode active substance of the present invention has a characteristic in that a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) and a fine particle as shown by the general formula LiFePO_4 are mixed and agitated at a particle temperature (T) in the range of $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$ in order to cover the surface of the above particle with the above fine particle.

[0015] In the manufacturing method of the above-mentioned positive electrode active substance of the present invention, by controlling the particle temperature during agitation of the particle mixture, the positive electrode active substance, in which the surface of the particle having the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ is covered with the fine particle having the general formula LiFePO_4 , is obtained.

[0016] Also, in the manufacturing method of the non-aqueous electrolyte battery of the present invention, a non-aqueous electrolyte battery comprising a positive electrode containing a positive electrode active substance, a negative electrode containing a negative electrode active substance and a non-aqueous electrolyte which is present between the above positive electrode and the above negative electrode is manufactured and this manufacturing method has a characteristic in that the positive electrode active substance is prepared by mixing a particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) and a fine particle as shown by the general formula LiFePO_4 and agitating the above particle mixture at a particle temperature (T) in the range of $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$ in order to cover the surface of the above particle with the above fine particle.

[0017] In the above-mentioned manufacturing method of the non-aqueous electrolyte battery of the present, the positive electrode active substance comprising the particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$, whose surface is covered with the fine particle as shown by the general formula LiFePO_4 , is obtained by controlling the particle temperature during agitation of the particle mixture. And using the manufacturing method of the non-aqueous electrolyte battery of the present invention in which such a positive electrode active substance is utilized, the non-aqueous electrolyte battery exhibiting high capacity and excellent charging/discharging cycle characteristics can be obtained.

[0018] [Mode of carrying out the invention]

In Figure 1, one example of the constitution of the non-aqueous electrolyte battery of the present invention is shown. This non-aqueous electrolyte battery 1 comprises a negative electrode 2, a negative electrode can 3 in which the negative electrode 2 is stored, a positive electrode 4, a positive electrode can 5 in which the negative electrode 4 is stored, a separator 6 which is disposed between the positive electrode 4 and the negative electrode 2 and an insulating gasket 7. The negative electrode can 3 and the positive electrode can 5 are filled with a non-aqueous electrolyte solution.

[0019] The negative electrode 2 consists of a negative electrode active substance such as lithium metal foil. Also, when a material which is capable of doping and undoping lithium is to be used as a negative electrode active substance, the negative electrode 2 has a configuration such that a negative electrode active substance layer containing the above-mentioned negative electrode active substance is formed on a negative electrode current collector. As the negative electrode current collector, for example, a nickel foil and the like are used.

[0020] As the negative electrode active substance which is capable of doping/ undoping lithium, a lithium metal, a lithium alloy and an electrically conductive polymer and a layered compound (carbon materials, metal oxides and the like) doped with lithium are used.

[0021] As the binder which is contained in the negative electrode active substance layer, conventional resin materials, which are normally

used as a binder for the negative electrode active substance layer in this type of non-aqueous electrolyte battery, can be used.

[0022] The negative electrode can 3 is used to store the negative electrode 2 and also serves an external negative electrode of the non-aqueous electrolyte battery 1.

[0023] The positive electrode 4 has a configuration such that a positive electrode active substance layer containing the positive electrode active substance is formed on a positive electrode current collector. As the positive electrode current collector, for example, an aluminum foil and the like, are used.

[0024] Here, in the present invention, as the positive electrode active substance, the particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co), whose surface is covered with the fine particle as shown by the general formula LiFePO_4 , is used.

[0025] As described above, the Ni composite oxide has a problem of exhibiting unstable structure and capacity fade due to a loss of large amounts of lithium during charging, although it has a high energy density. On the other hand, LiFeO_4 exhibits excellent structural stability and a lower degree of capacity fade. However, it has a problem of low energy density, which makes it difficult to be used alone.

[0026] The Ni composite oxide whose structure is destabilized due to the loss of lithium during charging causes a capacity fade as a result of structural destruction at the interface of the non-aqueous electrolyte

solution inside the battery. In particular, the degree of capacity fade becomes larger at a high temperature (40 ~ 60°C). When the surface of this Ni composite oxide is modified with a heat-stable LiFePO_4 , the capacity fade at a high temperature is significantly reduced. This is considered to be due to the fact that the thermally stable LiFePO_4 prevents the structural destruction of the surface of the above composite oxide.

[0027] As described above, by using the above positive electrode active substance comprising the Ni composite oxide particle as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) whose surface is covered with the LiFePO_4 fine particle, the non-aqueous electrolyte battery 1 having characteristics of high energy density derived from the Ni composite oxide and structural stability during charging derived from LiFePO_4 , while suppressing the structural deterioration of the Ni composite oxide can be obtained and it exhibits high capacity and excellent charging/discharging cycle characteristics.

[0028] As the binder which is contained in the positive electrode active substance layer, conventional resin materials which are normally used as a binder for the positive electrode active substance layer in this type of non-aqueous electrolyte battery can be used.

[0029] The positive electrode can 5 is to be used to store the positive electrode 4. Also, it serves as an external positive electrode of the non-aqueous electrolyte battery 1.

[0030] The separator 6 is used to physically separate the positive electrode 4 from the negative electrode 2. Conventional materials used as a separator in this type of non-aqueous electrolyte battery can be used. For example, a polymeric film such as polypropylene and the like, can be used. Also, from the standpoint of the relation between the electric conductivity of the lithium ion and the energy density, the film thickness of the separator is required to be as low as possible. Concretely, appropriate film thickness of the separator is, for example, 50 μm or less.

[0031] The insulating gasket 7 is placed in the negative electrode can 3 and integrated. This insulating gasket 7 is used for prevention of leakage of the non-aqueous electrolyte solution from the negative electrode can 3 and the positive electrode can 5.

[0032] As the non-aqueous electrolyte solution, a solution of an electrolyte dissolved in a non-protonic, non-aqueous solvent is used.

[0033] As the non-aqueous solvent, for example, propylene carbonate, ethylene carbonate, butylenes carbonate, vinylene carbonate, γ -butyrolactone, sulfolane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 2-methyltetrahydrofuran, 3-methyl-1,3-dioxolane, methyl propionate, methyl acetate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate and the like, can be used. In particular, cyclic carbonates such as propylene carbonate, vinylene carbonate and the like and linear carbonates such as dimethyl carbonate, diethyl carbonate, dipropyl carbonate and the like are preferable from the standpoint of voltage stability. Also, the

above non-aqueous solvents can be used alone or as a combination of at least 2 kinds.

[0034] Also, as examples of the electrolyte to be dissolved in a non-aqueous solvent, lithium salts such as LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and the like, can be mentioned. Among those lithium salts, LiPF_6 , LiBF_4 are preferably used.

[0035] As described above, in the non-aqueous electrolyte battery 1 of the present invention, the positive electrode active substance, comprising the Ni composite oxide particle having a general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) whose surface is covered with a LiFePO_4 fine particle, is used. As a result, the battery has characteristics of high energy density derived from the Ni composite oxide and structural stability during charging derived from LiFePO_4 , while suppressing the structural deterioration of the Ni composite oxide and it exhibits high capacity and excellent charging/discharging cycle characteristics.

[0036] Such a non-aqueous electrolyte battery is manufactured, for example, as follows.

[0037] Firstly, the positive electrode active substance of the present invention is manufactured.

[0038] To cause adherence of LiFePO_4 fine particle onto the surface of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle, for example, a method of so-called aqueous solution method, in which the above $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle is first treated

with a mixed aqueous solution of Fe or Li nitrate, ammonium phosphate and the like, then the treated particle is subjected to a heat treatment to form a layer of LiFePO_4 on the surface of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle, can be mentioned. In this aqueous solution method, a uniform LiFePO_4 surface layer can be obtained. However, a single LiFePO_4 phase cannot be obtained unless heat treatment is carried out under the reduction atmosphere. Furthermore, when the heat treatment is carried out under the reduction atmosphere, the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle is subjected to a structural destruction, causing a capacity fade. From the above standpoints, it is difficult to obtain the positive electrode active substance which can achieve the purpose of the present invention using this method.

[0039] On the other hand, as a dry application-type method which does not require the heat treatment, the particle hybridization method can be mentioned. In this particle hybridization method, particles with different particle sizes are mixed and agitated to generate static electricity by collision of particles and cause adherence of fine particles onto the surface of larger particles. Since this method does not involve a heat treatment step, surface modification of the particle can be carried out in the air. However, since the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle to be used in the present invention is fragile, it is prone to cracking by collision. The degree of collision cracking depends on hardness and particle size of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle, or hardness and particle size of LiFePO_4 , which adheres to the surface of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle. Therefore, the hybridization treatment

is required to be carried under the condition in which the collision cracking is suppressed.

[0040] The present inventors have done extensive research to find the condition under which the LiFePO_4 fine particle effectively adheres to the surface of the Ni positive electrode particle while suppressing the particle cracking and discovered that in the process of adherence of the LiFePO_4 fine particle to the surface of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle by the above particle hybridization method, excellent results can be obtained without generation of collision cracking of particle when the particle temperature T during the agitation treatment is in the range of $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$.

[0041] The above particle temperature T is an indicator in a quantitative monitoring of the degree of the collision of the particles during the agitation treatment. That is, since the particles are heated and the temperature of the particles increase by the energy generated by the collision between particles, controlling the particle temperature T has the same meaning as controlling the collision energy between particles.

[0042] Concretely, when the particle temperature T is lower than 35°C , the collision energy between particles is not sufficiently large. As a result, the LiFePO_4 fine particle cannot effectively adhere to the surface of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle. On the other hand, when the particle temperature T exceeds 45°C , the collision energy between particles becomes too large, causing collision cracking of the particle.

[0043] Therefore, by agitating a mixture of $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle and LiFePO_4 fine particle at a particle temperature T under the condition of $35^\circ\text{C} \leq T \leq 45^\circ\text{C}$, the LiFePO_4 fine particle can adhere to the surface of the $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ particle without causing the particle cracking and the positive electrode active substance of the present invention can be obtained.

[0044] Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery is manufactured as follows.

[0045] The positive electrode 4 is prepared as follows. A positive electrode active substance and a binder are dispersed in a solvent to prepare a slurry of the positive electrode mix. The obtained positive electrode mix is uniformly coated on a positive electrode current collector and dried to form a layer of the positive electrode active substance. After the above steps, the positive electrode 4 is manufactured. As the binder for the above positive electrode mix, conventional binders can be used. To the above positive electrode mix, conventional additives may be added.

[0046] To obtain the negative electrode 2, firstly, a negative electrode active substance and a binder are dispersed in a solvent to prepare a slurry of the negative electrode mix. The obtained negative electrode mix is uniformly coated on a negative electrode current collector and dried to form a layer of the negative electrode active substance. After the above steps, the negative electrode 2 is manufactured. As the binder for the above negative electrode mix, conventional binders can be used. To the above negative electrode mix, conventional additives may be added.

Also, a lithium metal, which is the negative electrode active substance, can be used as a negative electrode 2 by itself.

[0047] The non-aqueous electrolyte solution is prepared by dissolving an electrolyte salt in a non-aqueous solvent.

[0048] Then, the negative electrode 2 is stored in the negative electrode can 3 while the positive electrode 4 is stored in the positive electrode can 5. Between the negative electrode 2 and the positive electrode 4, a separator 6 based on a porous polypropylene film and the like is disposed. After the non-aqueous electrolyte solution is poured into the negative electrode can 3 and the positive electrode can 5, the electrolyte solution-filled negative electrode can 3 and positive electrode can 5 are pressed together through an insulating gasket and fixed to obtain a non-aqueous electrolyte battery 1.

[0049] In the above mode of carrying out the present invention, the non-aqueous electrolyte battery 1 which uses the non-aqueous electrolyte solution was described as an example of the non-aqueous electrolyte battery. However the present invention is not restricted to this. The present invention can be applied to a solid electrolyte battery which uses a polymeric solid electrolyte containing a single or a mixture of electrically conductive polymeric compounds and a gel-like electrolyte battery which uses a gel-like solid electrolyte containing a swelling solvent.

[0050] As concrete examples of the electrically conductive polymeric compound which is contained in the above polymeric solid electrolyte or

gel-like electrolyte, silicone polymers, acrylic polymers, acrylonitrile polymers, polyphosphazene-modified polymers, polyethylene oxide, polypropylene oxide and fluorinated polymers, and their composite polymers, crosslinked polymers, and modified polymers and the like, can be mentioned. As examples of the above fluorinated polymers, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinylidene fluoride-co-tetrafluoroethylene), poly(vinylidene fluoride-co-trifluoroethylene) and the like, can be mentioned.

[0051] Also, in the above mode of carrying out the present invention, the secondary battery was used as an example. However, the present invention is not restricted to this. The present invention can be also applied a primary battery. Also there is no restriction on the shape of the battery in the present invention. For example, a battery may have a cylindrical shape, rectangular shape, coin shape, button shape or the like. Also, a battery may have various sizes, such as a thin-type, larger size-type or the like.

[0052] [Example]

The effects of the present invention were confirmed by examples and comparative examples as follows. In the examples below, explanations were made using concrete numerical numbers. However, the present invention will not be restricted to these.

[0053] <Example 1>

The positive electrode active substance of the present invention was synthesized as follows.

[0054] Firstly, 30.0 g of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and 1.0 g of LiFePO_4 fine particle were mixed. Here, the median diameter of the used $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle was 11.458 μm , while that of LiFePO_4 fine particle was 0.185 μm . The particle size distribution curves of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle were shown in Figure 2 and Figure 3, respectively.

[0055] Subsequently, a mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle was agitated for 5 minutes to cause adherence of the LiFePO_4 fine particle onto the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle for surface modification. After the above process, a positive electrode active substance was obtained. In the above process, agitation of the particle mixture was carried out using a hybridization system NHS-O from Nara Machine Co. The rotation speed was controlled such that the treatment temperature T would be 36°C.

[0056] Next, a coin-type non-aqueous electrolyte battery was manufacture using the obtained positive electrode active substance.

[0057] The obtained positive electrode active substance in an amount of 80 wt.% (based on the dry weight), graphite (average particle size from 5 μm to 20 μm ; trade name KS-15 Lonza) as an electrically conductive agent in an amount of 15 wt.% and polyvinylidene fluoride (Aldrich #1300) as a binder were kneaded using dimethyl fluoride to obtain a positive electrode paste.

[0058] This positive electrode paste was coated on an aluminum mesh which was used as a positive electrode current collector, pelletized together with the aluminum mesh, and dried at 100°C for 1 hour under the flowing dry argon gas to obtain a positive electrode. This positive electrode contained 60 mg of the positive electrode active substance per 1 sample.

[0059] Also, a negative electrode was prepared by punching a lithium metal in almost the same size as the above positive electrode.

[0060] To an equivolume mixture of propylene carbonate and dimethyl carbonate, LiPF_4 was dissolved in a concentration of 1 mol/l to obtain a non-aqueous electrolyte solution.

[0061] The obtained negative electrode was stored in the negative electrode can, while the positive electrode was stored in the positive electrode can. Between the negative electrode and the positive electrode, a separator based on a porous polypropylene film and the like, was disposed. The non-aqueous electrolyte solution was poured into the negative electrode can and the positive electrode can and the both cans were fixed by tightly pressing to each other through the insulating gasket to obtain a 2025 coin-type non-aqueous electrolyte battery.

[0062] <Example 2>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become

38°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0063] <Example 3>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become 40°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0064] <Example 4>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become 42°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0065] <Example 5>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become

44°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0066] <Comparative Example 1>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become 30°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0067] <Comparative Example 2>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become 34°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0068] <Comparative Example 3>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become

46°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0069] <Comparative Example 4>

A positive electrode active substance was synthesized following the same procedure as described in Example 1, except that during agitation of the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle, the rotation speed was adjusted so that the particle temperature T would become 50°C. Using the obtained positive electrode active substance, a coin-type non-aqueous electrolyte battery was manufactured following the same procedure as described in Example 1.

[0070] <Comparative Example 5>

A coin-type non-aqueous electrolyte battery was prepared following the same procedure as described in Example 1, except that the above $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle was used as the positive electrode active substance without surface modification treatment of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle.

[0071] The load characteristics of each of the obtained non-aqueous electrolyte batteries were measured. Initial charging was carried out until the open circuit voltage (OCV) reached 4.2 V +/- 0.05 V at the current density of 500 $\mu\text{A}/\text{cell}$. Also, discharging was carried out until the closed circuit voltage (CCV) reached 3.0 V at the current density of 500 $\mu\text{A}/\text{cell}$.

[0072] Furthermore, charging was carried out until OCV reached 4.2 V and the battery was stored at 60°C for 24 h. After the completion of

storage, discharging was carried out under the same conditions as the initial cycle at the same current density to measure the capacity.

[0073] The degree of capacity retention was calculated from the discharge capacity before storage, abbreviated as $C_{ap}(A)$, and the discharge capacity after storage, abbreviated as $C_{ap}(B)$, using the equation as shown below:

$$[0074] \text{ The degree of capacity retention (\%)} = \{C_{ap}(B) / C_{ap}(A)\} \times 100$$

In Figure 4, the relationship between the particle temperature T during agitation of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle and the degree of the capacity retention (%) of the non-aqueous electrolyte battery was constructed from the results of the non-aqueous electrolyte batteries of Examples 1 ~ 5 and Comparative Examples 1 ~ 5. In Figure 4, a horizontal dotted line indicates the degree of capacity retention (%) of the battery in Comparative Example 5 in which the surface modification of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle was not carried out.

[0075] As obvious from Figure 4, batteries of Comparative Example 1 and Comparative Example 2, in which the particle temperatures T during agitation of the mixture of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle and LiFePO_4 fine particle were lower than 35°C, had a lower degree of capacity retention than that of the battery of Comparative Example 5, in which the surface modification of the particle was not carried out. This is considered to be due to the fact that since the collision energy between particles was not sufficiently large in the above cases, the LiFePO_4 fine particles did not successfully adhere to the surface of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles.

[0076] Also, the batteries of Comparative Examples 3 and Comparative Example 4, in which the particle temperatures T were 45°C or higher, had a lower degree of capacity retention than the battery of Comparative Example 5. This is considered to be due to the generation of collision cracking of the particles since the collision energy between particles was too large.

[0077] On the other hand, the batteries of Examples 1 ~ 5, in which the particle temperatures T satisfied the condition of $35^{\circ}\text{C} \leq T \leq 45^{\circ}\text{C}$, had far better degree of capacity retention than the battery of Comparative Example 5. This is considered to be due to the fact that since the collision energy between particles was appropriately controlled in the above cases, LiFePO_4 fine particles successfully adhered to the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles without causing particle cracking. The non-aqueous electrolyte batteries using such positive electrode active substances exhibited high capacity and excellent charging/discharging cycle characteristics.

[0078] [Effect of the invention]

In the present invention, since the particle surface of a Ni composite oxide as shown by the general formula $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (wherein in this formula, M represents elements containing at least 1 kind selected from Al, B and Co) is covered with an LiFePO_4 fine particle, a resultant positive electrode active substance has favorable characteristics of high energy density derived from the Ni composite oxide and excellent structural stability during charging derived from LiFePO_4 , while suppressing the structural deterioration of the Ni composite oxide. By using this positive electrode active substance, a non-aqueous electrolyte battery exhibiting high

capacity and excellent charging/discharging cycle characteristics can be obtained.

[Brief explanation of the invention]

[Figure 1] This is a cross-sectional view of an exemplified non-aqueous electrolyte battery of the present invention.

[Figure 2] This is the figure showing the particle size distribution curve of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particle used in the examples.

[Figure 3] This is the figure showing the particle size distribution curve of the LiFePO_4 fine particle used in the examples.

[Figure 4] This is the figure showing the relationship between the particle temperature T during agitation of the particle mixture and the degree of the capacity retention of the batteries obtained in the examples.

[Explanation of the symbols]

1. Non-aqueous electrolyte battery
2. Negative electrode
3. Negative electrode can
4. Positive electrode
5. Positive electrode can
6. Separator
7. Insulating gasket

Figure 1

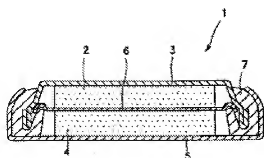
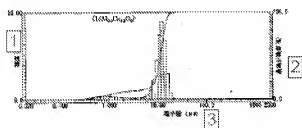


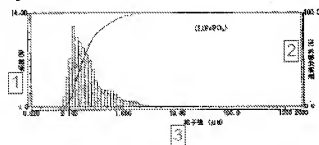
Figure 2



Key:

- 1) Frequency (%)
- 2) Cumulative passage distribution (%)
- 3) Particle size (μm)

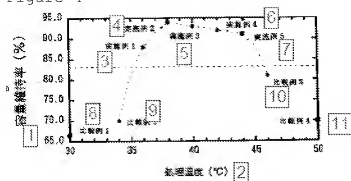
Figure 3



Key:

- 1) Frequency (%)
- 2) Cumulative passage distribution (%)
- 3) Particle size (μm)

Figure 4



Key:

- 1) Degree of capacity retention (%)
- 2) Treatment temperature (°C)
- 3) Example 1
- 4) Example 2
- 5) Example 3
- 6) Example 4
- 7) Example 5
- 8) Comparative Example 1
- 9) Comparative Example 2
- 10) Comparative Example 3
- 11) Comparative Example 4